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Quality aspects of fish and fishery products in catching, storage and processing.

by

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Svensk Veterinärtidning (Swedish Veterinary Journal) 1982, 34, (16): 735-740.

The article describes fish as a raw material and discusses the opportunities and limitations for directly utilizing or further processing the raw material for frozen consumer products. The author describes the biochemical, physical and microbiological changes in fish and fishery products that are of importance for quality.

p. 735

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Fish live in the wild, and individual species and seasonal changes will always be reflected in natural quality variations. In addition, area of catch and food selection can cause large variations in appearance and taste of fish of the same species but from different areas. Fishing methods and onboard handling can also be of considerable importance for raw material quality.

In fresh fish the temperature is the decisive factor for quality and shelf-life. In fresh, ungutted fish, autolysis starting in the gut cavity is also a factor limiting keeping time. In gutted and filleted fish, the critical factors are rancidity for fatty fish and bacterial activity for lean fish.

In frozen fishery products, protein denaturation, fatty acid oxidation and also lipolysis are factors limiting long-term storage. Autolytic rancidity dominates in fatty fish while texture changes through protein denaturation are serious problems in lean fish.

Biological and physiological factors of technological importance

The fish muscle - biological and physiological characteristics.

The muscles of fish are located in two large bundles (fillets) on each side of the skeleton. The musculature is common striated musculature of two different types normally designated as light and dark. The light musculature, which most often comprises the bulk of the muscles, is usually white or has a greyish or yellowish cast. The dark muscle

is brown or reddish brown as a result of a greater flow of blood.

The dark muscles are located along the outside of the fillets, and the amount varies from species to species depending on the behavior pattern. In species like herring, mackerel and pollock, which are actively swimming almost continuously, the dark muscle can comprise up to 50% of the total muscle. However, in flat fish, which rest on the bottom for long periods, the dark muscle comprises only two percent or so.

There are several differences in chemical composition between the two muscle types, but of greatest importance is the higher fat content in the dark muscle. Average composition is for most fish species within the following limits:

Protein	17-19%
Carbohydrates	Max. 1%
Water	60-80%
Fat	1.2 - 25%

The contents of protein and carbohydrate are relatively constant and species-specific, while, in contrast, the fat and moisture content can vary considerably; not only between species, but also within the same species depending on season. p.736

The protein consists of sarcoplasmatic proteins (20-35%), actin, myosin and actomyosin (65%) and stroma protein (3-8%). This is very similar to other animal proteins.

The fat (lipid) is different in several respects from

other animal or vegetable fats. More than one third consists of long-chain fatty acids with 18 carbon atoms or more. Most of the C_{20} and C_{22} fatty acids have 5 or 6 double bonds. A high unsaturation like that is characteristic of marine lipids.

The distribution of fat in the body varies from species to species and also within species depending on season. In fatty fish there is normally a thick layer of fat under the skin. In lean fish the fat is chiefly concentrated in the dark muscles and in non-triglycerides in cell walls. In general, the dark musculature and the belly and fin musculature have higher lipid contents than the rest of the muscles.

The water content is usually closely related to the fat content, since these two components always add up to about 80%. Fatty fish therefore contain less water than lean fish, and annual variations in fat contents are inversely proportional to the water content. However, the water content can vary by a couple of percents seasonally, also in lean fish.

Annual variations can be related to the life cycle of the species. During the spawning season, which in our waters most often is in the spring or early summer, the fish do not eat and utilize energy reserves in the muscles and liver for gonad development. The general condition of the fish deteriorates sharply, the water content increases and the fat content drops, in fatty fish often from 25-30% down to 3-4%. In this period the quality of the fish flesh is lowered considerably, especially the texture, which

becomes more jelly-like or watery. Figure 1 shows the annual variations in fat content in mackerel.

Fish-muscle composition is also characterized by a high content of non-protein nitrogen (NPN). This can comprise 9-18% of the total nitrogen content. Dark muscle has the highest content of these substances, and species variation therefore depends to a large extent on the percentage of dark muscle in the fish. NPN - substances consist typically of ammonia, trimethylamines (TMA), trimethylamine oxide (TMAO) and amino acids.

NPN substances play an important role in the characteristic flavor of the fish, but also in quality changes occurring in fresh fish.

Postmortal changes in fresh fish.

Sensory

Newly caught fish have a bright and shiny surface with firm and transparent slime. The eyes are clear and protruding, the gills are bright red, odor is neutral or fresh seaweed-like. During storage the slime layer gradually thickens and becomes opaque. The eyes sink into the head and become covered with a cloudy slime. The gills are bleached, at times with a yellow discoloration and are covered with a thick layer of slime. The odor changes from neutral to acidy and then to ammoniacal and hydrogen sulfide-like. The texture of the flesh changes from firm and elastic to soft and doughy.

Biochemical

Rigor mortis occurs normally relatively quickly after the death of the fish, but the low glycogen content prevents the pH from dropping more than from ca. 7 to 6.2-6.5. The rate of energy breakdown depends on species, size, condition, and degree of exhaustion. In general the process is faster in small, active fish like herring, mackerel and sprat. In cod and flatfish kept at 0-3°C, the rigor process is normally completed in 1-3 days after catch. p.737

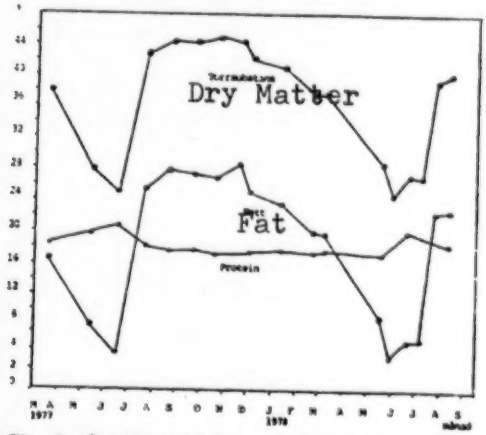

Fig. 1. Årstidsvariationer i sammansättningen av makrill, mars 1977–augusti 1978.

Fig. 1. Annual variations in composition of mackerel, March 1977-August 1978.

Shortly after the death of the fish, the breakdown of nucleotides in the flesh starts. The breakdown of nucleotides occurs through autolytic dephosphorization and deamination of adenine triphosphate (ATP) to hypoxathine (Hx) via inosine monophosphate (IMP) and inosine (In). The

conversion of ATP to IMP proceeds relatively quickly in the first 24 hours. IMP has a flavor-enhancing effect and is thought to be responsible for the characteristic sweet, seaweed-like odor and taste so typical for newly caught fish. Hx is bitter and is detected as an unpleasant and old flavor in fresh fish. The rate of nucleotide breakdown is strongly temperature-dependent. The rate as well as the level of the material formed are also species-specific.

Changes in fatty fish in cold storage are largely due to hydrolysis and oxidation of the fat which is very unstable due to the high degree of unsaturation. Hydrolysis is enzymatic and especially associated with stomach contents, and it is therefore of importance in fish brought ashore ungutted. Autoxidation, when unsaturated fatty acids are broken down to peroxides with the formation of aldehydes and ketones, results in a yellowish discoloration of flesh and fat and a noticable rancid taste and odor. The rate of autoxidation is strongly dependent on temperature and light. Great care in handling the catch is therefore the most essential condition for preventing this quality deterioration.

Microbiological

Newly caught fish normally have a bacterial count of 10^2 - $10^6/cm^2$ on the skin surface and somewhat higher on the gills while the meat and the inside of the fish are normally sterile. The surface flora and composition are determined by external factors such as water temperature, degree of contamination, catching method and season. In our northern

waters the flora consists chiefly of gram -negative psychrophilic types of Pseudomonas, Flavobacterium, Acinetobacter, Moraxella and Vibrio.

Microbiological activity is the chief storage-limiting factor in fresh, lean fish. During storage at 0°C the bacterial count increases to 10^7-10^9/cm^2 in 9-10 days. Simultaneously the composition of the flora changes so that Pseudomonas spp become dominant.

Common for the dominant species is that they can utilize naturally occurring NPN-sources such as TMAO, nucleotides and amino acids as well as the reaction products inosine, hypoxanthine and lactate.

In summary, the bacterial activity can be described as follows: After an incubation period of 5-6 days (at 0°C), bacterial growth accelerates. At an early stage there is a selection towards certain Pseudomonas species that can utilize naturally occurring NPN-compounds, especially P. putrefaciens, P. putida and P. fluorescens. These species oxidize amino acids and lactic acid to esters with sweet or fruity odors and reduce trimethylamine oxide (TMAO) to TMA which gives the characteristic strong fishy odor. In a later stage, sulphur-containing amino acids are broken down to volatile sulphur compounds such as hydrogen sulphide, methyl sulphide and methyl mercaptan, and ammonia is formed as a result of the proteolysis. It is therefore bacterial activity that first and foremost is responsible for development of the disagreeable odors and flavors which limit the shelf-life of fresh fish.

The level of TMA or the total amount of volatile bases (TVB) can be used as quality parameters for many fish species. However, the amounts of TMA/TVB, as well as rate of formation, are species-specific, and there is in general no clear correlation between the content of TMA or TVB and the eating quality. Newly caught cod contains about 1-1.5 mg TMA-N/100g while an unacceptable quality contains about 8-15 mg.

Factors influencing quality and keeping time of fresh fish.

Temperature

The decisive factor in determining the keeping time of fish is the storage temperature. Characteristic of fish is also that a temperature in the range 0-5°C is of decisive importance for biochemical and bacteriological decomposition processes. The time required for cod and plaice to be completely spoiled is twice as long at 0°C as at 4.4°C. As a rule of thumb the following keeping times for cod are considered typical:

p.738

Temperature, °C:	0	0.5	3	7	10
Keeping time, days:	11-12	6-8	5-6	2-3	20-30 hrs

It can be seen that an effective temperature control immediately after catch is very important. A short period with insufficient temperature control can be enough to ruin the quality of the fish. For example, it has been shown for

herring that by waiting for 4-6 hours before icing, the keeping time is cut in half, especially due to rancidity. Lean fish and flatfish also exhibit a similar, but less pronounced tendency.

In cool storage of fish, the skin must always be kept moist since dehydration accelerates the oxidation processes. The common chilling methods are therefore based on ice, ice and water, or mechanically refrigerated water as the cooling medium. The different methods affect the quality differently depending on fish species, storage time and how effectively they are carried out.

Bleeding and gutting.

Effective gutting, bleeding and chilling immediately after catching are of decisive importance for quality and keeping time for most species. The reason is that digestive enzymes continuing their activity in the gut (autolysis) quickly result in noticable changes in smell, taste and appearance, first in the gut cavity and later in the whole musculature. For both cod and plaice, the quality deterioration resulting from poor gutting will show up already during the first 24 hours and the total keeping time will be halved. For species like haddock, whiting and pollock the tendency is the same but less pronounced.

For quality reasons most species should therefore be gutted within a few hours after catch. The exception is small species like herring and mackerel which are normally landed

in such large quantities that gutting is impossible. Especially in the summer when stomachs are well filled and enzyme activity high, it can be observed that the bellies of many fish will burst; i.e. the stomach wall is eaten through and the stomach contents spread over the rest of the fish. The fish will then spoil rapidly. In this period rapid icing is of decisive importance if an acceptable raw material quality is to be achieved.

As part of the gutting operation, the throat and main arteries of the fish are normally cut so that the fish can bleed. It is equally important that this is carried out quickly. Otherwise blood will penetrate the flesh and give a reddish discoloration. This is a quality deterioration in itself, and it will also result in shorter keeping time since blood pigments promote fat oxidation and therefore development of off-flavors and rancidity. In practice, throat cutting and gutting are normally carried out together with generally satisfactory results. The best results are obtained if the throat cutting is carried out while the fish are still alive, and especially if the cut is deep enough to cut the dorsal main arteries in the neck and also in the gills.

Quality and quality changes in frozen fish products.

Sensory and biochemical changes

Sensory.

Quality changes during frozen storage of fish are normally described in one or more of the following terms.

Taste and odor become acidic, bitter, lye-or cabbage-like in lean fish and soapy, oily or rancid in fatty fish. The texture becomes firm, hard, tough, spongy or dry. Appearance is often dull, opaque and greyish yellow in white fish, in fatty fish a yellow or reddish brown discoloration of the fat can been seen.

Protein

Protein denaturation is the main cause of texture changes during frozen storage of fish. The denaturing process in frozen fish is still not completely known, but it appears to be clear that it involves reactions between protein and enzymatic reaction products formed during storage. Free fatty acids and oxidation products of these and also formaldehyde are examples of materials that react with proteins. The exact mechanisms appear to be species-specific. Formaldehyde has been shown to be of decisive importance in many species of the cod family, while in other species, such as mackerel and flatfishes, no formaldehyde was formed at all. p.739

Fat

Autoxidation and enzymatic hydrolysis are responsible for changes in lipids. Fatty acids are formed through hydrolysis, and these can eventually affect protein denaturation. However, otherwise it is uncertain how these changes affect the acceptability of frozen products.

In fatty fish, rancidity as a result of autoxidation is always the most important limiting factor in cold storage. In cod it appears that the characteristic cold storage flavor

is correlated with the formation of a specific by-product of autoxidation.

Factors of importance for quality and keeping time in frozen, filleted products.

Species variation.

The rates and character of quality changes are more or less species-specific. The variations are primarily related to fat content and fat composition, but can also to a certain degree be caused by the various mechanisms for protein denaturation. Some typical storage times for various fish species are shown in Table I.

Table I

Typical storage times for single-frozen (IQF) fillets of various fish species at -20°C.

Species	Keeping time, months
Cod	min. 18
Plaice	10-13
Herring	4-6
Flounder	6-9
Pollock	12-15
Mackerel	3-5

In lean fish where the lipids are chiefly found as non-triglycerides, the autoxidation is much slower than in fatty fish where autoxidation chiefly takes place in the

triglycerides. Other factors also can influence the flavor changes such as the combination of fatty acids and their relative location in the glyceride molecules and the presence of anti- or pro-oxidative material.

Rigor mortis/pH

It is well known that the best fillet products are those that are filleted immediately after rigor mortis. Fillets cut before rigor mortis will contract during handling before freezing or during thawing. This shrinkage will give an uneven and ragged appearance to the fillets in that fillet segments are displaced relative to each other (called gaping). Toughness and drip losses increase. This problem is only present when filleting and/or freezing takes place onboard. When the fish have reached shore, rigor has usually set in.

Fish that are frozen whole and later thawed and filleted are acceptable even if freezing takes place pre-rigor, since the muscles are still fastened to the skeleton and therefore cannot contract much during rigor.

Biologically defined variations such as fish age, size, condition and pH can also have a certain influence on the physical quality of frozen products.

Freezing time and storage temperature.

When freezing fish, it is important to pass the interval from -2 to -5°C as quickly as possible, since lipolysis and autoxidation take place at a maximum rate in this temperature range. Otherwise the freezing temperature, except in extreme cases, will not have a major influence on the final quality.

Storage temperatures are, however, of major importance for the storage life of the products. A lowering of the temperature from for example -20° to $-30^{\circ}C$, will double the storage life of most fish species. Large variations in the storage temperature have considerable influence on the total storage life of the product. In a storage experiment at $-18^{\circ}C$ for 45 weeks, it was found that the amount of extractable protein as well as the sensory quality dropped considerably if the product was stored for two weeks at -9° or $-12^{\circ}C$. The drop in quality manifested itself only in the following month at a normal storage temperature.

Oxygen.

The presence of oxygen is of great importance for the storage life of fatty fish. With normal packaging, freezing and frozen storage, herring only has a storage life of 5-6 months. By vacuum packaging in film with low air penetration and by packing in controlled atmosphere (N_2 or Co_2), the storage life can be doubled as long as the raw material quality is good. p.740

Other treatments that protect against the negative affect of air are treatments with ascorbic acid, which has an antioxidative effect, or covering the fish with sauce which has almost the same effect as vacuum packaging.

It should also be mentioned that the rate of oxidation varies not only between species but also within the same species. In England it was found that the degree of unsaturation in mackerel fat varies according to season and

that this indicates differences in the rate of oxidation. Experiments in Denmark demonstrated a considerable difference between individual fish in the same catch. In contrast to these results, it was found at Nordreco in 1969 that the storage life of herring only to a limited extent was affected by seasonal variations in fat contents of 3-20%.

In general it can be stated that processing of frozen products from fatty fish still has many problems: problems that can be controlled to a certain degree but which almost always require individual solutions depending on fish species, type of product and storage time requirements.

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